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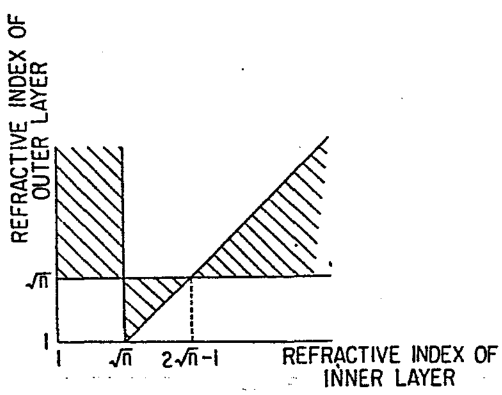
(54) An anti-reflection coating for an infrared transmitting material and laser beam transmitting window or fiber incorporating the same.

(57) An anti-reflection coating for an infrared transmitting material, which is stable to water or moisture and free from deterioration in performance for a long period of time, comprises an inner layer of an alkali metal halide and an outer layer, provided thereon, of an infrared transmitting material, the inner layer and outer layer being provided on a substrate of the infrared transmitting material and having refractive indexes falling within the shaded portion in the accompanying figure, n representing the refractive index of the substrate.

FIG. 2



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AN ANTI-REFLECTION COATING FOR AN INFRARED TRANSMITTING MATERIAL AND LASER BEAM TRANSMITTING WINDOW OR FIBER INCORPORATING THE SAME

This invention relates to an anti-reflection coating for an infrared transmitting material. More particularly it is concerned with an anti-reflection coating film provided for inhibiting the loss due to reflection in an infrared transmitting material.

Crystalline materials, for example, silver halides such as silver bromide and silver chloride, thallium halides such as KRS-5 and KRS-6 and alkali halides such as cesium iodide and cesium bromide, well known as infrared transmitting materials, have been considered full of promise as CO_2 laser beam transmitting window materials or CO_2 laser beam transmitting fibers. However, these materials each have a large refractive index at the wavelength of 10.6 µm of µm of a CO_2 beam and, accordingly, the incident beam on the surface has a large reflectivity. In Table 1 are shown the refractive indexes and reflectivities of these materials at a wavelength of 10.6 µm of a CO_2 laser beam:

Table 1

Materials	Refractive Index n	Reflectivity (%)	$\sqrt{n}$
Silver Bromide	2.17	13.6	1.47
Silver Chloride	1.98	10.8	1.41
KRS-5*	2.37	16.5	1.54
KRS-6*	2.17	13.6	1.47
Cesium Iodide	1.74	7.3	1.32

Note: *) KRS-5(commercial name): mixed crystal of 45.7 % TlBr + 54.3 % TlI

KRS-6(commercial name): mixed crystal of 40 % TlBr + 60 % TlCl

These materials have a reflectivity of more than 7. Thus, it is important to reduce the reflective loss and to raise the transmission of a window or fiber. As a method of reducing reflective loss, it is known to form a non-reflective coating film. In a non-reflective coating monolayer, the reflectivity can be made zero by forming on the surface of a substrate a coating film consisting of a material with a refractive index equal to the square root $\sqrt{n}$ of the refractive index n of the substrate to a thickness of $d = \lambda/4n$ wherein λ is the wavelength of the transmitted light. The square root $\sqrt{n}$ of the refractive index of the above described materials is in the range of 1.3 to 1.6 as shown in Table 1. As a material transparent in the infrared region and having a refractive index of 1.3 to 1.6, there are potassium bromide, potassium chloride, sodium chloride, sodium fluoride, calcium fluoride and barium fluoride. These materials have reflective indexes and absorption coefficients at a wavelength of 10.6 µm as shown in Table 2:

Table 2

Material	Refractive Index	Absorption Coefficient cm^{-1}
Potassium Bromide	1.53	4.2×10^{-4}
Potassium Chloride	1.45	1.4×10^{-4}
Sodium Chloride	1.49	4.5×10^{-4}
Sodium Fluoride	1.23	5×10^{-2}
Calcium Fluoride	1.31	3.5
Barium Fluoride	1.42	0.19

The reflectivity can be decreased to less than about 3 % by forming a film of these materials with a thickness of $\lambda/4n$ on the surface of silver bromide, silver chloride, KRS-5, KRS-6 or cesium iodide. However, calcium fluoride and barium fluoride each have a relatively large absorption coefficient as shown in Table 2 and are not suitable for use in transmitting a high output CO_2 laser beam since their coatings tend to be damaged due to absorption. On the other hand, potassium bromide, potassium chloride, sodium chloride and sodium fluoride are all deliquescent, although their absorption coefficients are sufficiently small, so coatings thereof tend to take in moisture from the air and readily decompose and cannot be used as anti-reflection coatings in stable manner for a long period of time.

The present invention aims to avoid these problems and to provide an anti-reflection coating film capable of decreasing the reflective loss of an infrared transmitting material, specifically to provide an anti-reflection coating capable of preventing an infrared transmitting material such as silver bromide or silver chloride from showing a decrease in the transmission of light.

The invention thus provides an anti-reflection coating for an infrared transmitting material comprising two layers, an inner layer of an alkali metal halide and an outer layer, provided thereon, of an infrared transmitting material, the refractive indexes of the inner layer and outer layer being in the range of the shaded portion of Fig. 2, in which n is the refractive index of the substrate of infrared transmitting material.

The accompanying drawings are given to illustrate the principle and merits of the present invention in greater detail.

Fig. 1 is a cross-sectional view of one embodiment of an infrared transmitting material provided with an anti-reflection coating according to the present invention.

Fig. 2 is a graph showing the conditions under which the reflectivity is zero when providing a substrate with two layers of anti-reflection coatings.

The present invention is based upon the finding that if a coating consisting of a material capable of reducing the reflective loss but having a large solubility in water, such as potassium bromide, potassium chloride, sodium fluoride or sodium chloride, is covered with another coating consisting of an infrared transmitting material stable to water, the inner layer is protected from water and the outer protective layer may be caused to play a role as the outer layer of an anti-reflective double layer but not so as to decrease the anti-reflection effect. Furthermore, the present invention aims at preventing a substrate of silver bromide or silver chloride from a decrease in the transmission of light by protecting the substrate from irradiation by visible rays and ultraviolet rays using a material opaque to visible rays and ultraviolet rays as the outer layer (since silver bromide or silver chloride has a tendency to decompose under irradiation by visible rays and ultraviolet rays).

Accordingly, the present invention provides an anti-reflection coating film for an infrared transmitting material, consisting essentially of an inner layer of an alkali metal halide and an outer layer, provided on the inner layer, of an infrared transmitting material, the inner layer and outer layer being provided on a substrate of the infrared transmitting material and having refractive indexes within the shaded portion in Fig. 2, n representing the refractive index of the substrate. Generally, this anti-reflection coating is provided on the surface of a substrate consisting of an infrared transmitting material such as a silver halide, thallium halide or alkali metal halide, or on the input or output end of an infrared fiber consisting of the same material.

In the case of an anti-reflection coating of double layer structure, in general, it is known that the reflectivity can be zero when the combination of refractive indexes of the inner layer and outer layer is in the range of the shaded portion of Fig. 2 in relation to the refractive index n of the substrate (K. Schuster, Ann. Phys., Sixth Ser. 4 352 (1949)).

In the present invention, as the substrate there there may be used indexes n as shown in Table 1, $\sqrt{n}$ being in the range of 1.3 to 1.6, for example, silver halides such as silver bromide, silver chloride and mixed crystals thereof, thallium halides such as thallium chloride, thallium bromide, thallium iodide and mixed crystals thereof and alkali metal halides such as cesium iodide, cesium bromide and mixed crystals thereof. As the inner layer of the anti-reflection coating provided on such a substrate, there may be used alkali metal halides whose refractive index is in the same range as the above material $\sqrt{n}$, while as the outer layer of the anti-reflection coating there may be used infrared transmitting materials which are stable to water and whose refractive indexes are, in combination with the refractive index of the inner layer, in the range of the shaded portion of Fig. 2, thereby making the reflectivity zero, for example, silver bromide, silver chloride and mixed crystals thereof, thallium chloride, thallium bromide, thallium iodide and mixed crystals thereof, lead fluoride, zinc sulfide, zinc selenide and the like. In addition, germanium, silicon, cadmium telluride and gallium arsenide, which are stable to water and capable of forming a hard film opaque to visible rays and ultraviolet rays, are also suitable for use as a material for the outer layer as set forth above, and when using these materials, the effect of preventing the substrate from decomposition due to visible rays and ultraviolet rays is additionally achieved.

The inner layer and outer layer can be provided on a substrate, for example, by a vapor deposition method.

The refractive indexes at a wavelength of 10.6 μm and the transmitting wavelength region of outer layer materials are shown in Table 3:

Table 3

Outer Layer Material	Refractive Index	Transmitting Wave-length Region (μm)
Silver Bromide	2.17	0.5-30.0
Silver Chloride	1.98	0.4-30.0
KRS-5	2.37	0.5-40.0
KRS-6	2.17	2.0-20.0
Lead Fluoride	2.18	0.3-10.0
Zinc Sulfide	2.20	0.5-15
Zinc Selenide	2.42	0.5-25
Germanium	4.00	1.8-22
Silicon	3.42	1.2-13
Cadmium Telluride	2.67	0.91-15
Gallium Arsenide	3.10	1.0-11

The materials described in Table 3 are all stable to water or moisture and capable of forming a protective layer for a deliquescent inner layer. Above all, germanium, silicon, cadmium telluride and gallium arsenide do not permit visible rays or ultraviolet rays and when using these materials as an outer layer material in the non-reflective coating for light-sensitive materials such as silver chloride and silver bromide, therefore, a substrate of silver chloride or silver bromide can effectively be protected from decomposition.

As the present coating material having an inner layer and an outer layer, there can be used any combination of the alkali metal halides described in Table 2 and the materials described in Table 3, which have refractive indexes in the range of the shaded portion of Fig. 2.

The following Examples are given in order to illustrate the present invention in detail without limiting the same.

Example 1

Referring to Fig. 1, a silver bromide crystal plate 1 is provided with an anti-reflection coating consisting of inner layer 2 of potassium chloride and an outer layer 3 of silver bromide by a vacuum vapor-deposition method. As to the refractive indexes of the substrate and the inner layer and outer layer of the anti-reflection coating, silver bromide has a refractive index n of 2.17, $\sqrt{n}$ being 1.47, so the combination of potassium chloride in inner layer 2 (refractive index at a wavelength of 10.6 μm = 1.45) and silver bromide in outer layer 3 (refractive index at a wavelength of 10.6 μm = 2.17) is in the range the shaded portion of Fig. 2, thus making the reflectivity zero.

Since inner layer 2 of Fig. 1, consisting of deliquescent potassium chloride, is completely covered with outer layer 3 consisting of silver bromide (which is stable to moisture), the anti-reflection coating is stable to moisture and capable of maintaining the initial non-reflective effect for a long period of time without being decomposing.

The film thickness of each layer can be determined by the following conditions ("Usumaku Kogaku (Thin Film Engineering) Handbook" published by Ohm Co., p-II-297):

$$A + nB - C - nD = 0$$

Herein,

$$A = \cos\delta_1 \cos\delta_2 - \frac{n_2}{n_1}\sin\delta_1 \sin\delta_2$$

$$B = i\left(\frac{1}{n_2}\cos\delta_1 \sin\delta_2 + \frac{1}{n_1}\sin\delta_1 \cos\delta_2\right)$$

$$C = i(n_1\sin\delta_1 \cos\delta_2 + n_2\cos\delta_1 \sin\delta_2)$$

$$D = \frac{n_1}{n_2}\sin\delta_1 \sin\delta_2 + \cos\delta_1 \cos\delta_2$$

$$(i = \sqrt{-1})$$

$\delta_1 = \frac{2\pi}{\lambda} n_1 d_1$ (n_1, d_1: refractive index, film thickness of outer layer)

$\delta_2 = \frac{2\pi}{\lambda} n_2 d_2$ (n_2, d_2: refractive index, film thickness of inner layer)

(λ : wavelength of light used)

In this Example, the inner layer was provided at a thickness of 1.82 μm and the outer layer, at a thickness of 2.41 μm to give a reflectivity of less than 1 %.

For the purpose of examining the effect of this double layer coating, a similar silver bromide crystal plate was coated with only one layer of potassium chloride with a thickness of 1.82 μm by a vacuum vapor deposition method and compared with the above described double layer coating.

In the case of the monolayer coating, the reflectivity was only less than 1 % immediately after coating, but after being allowed to stand in humidity of 60% at room temperature for two days the coating film became slightly opaque and the transmission of a CO_2 laser beam was lowered from the initial 99 % to 80 %. In the case of the double layer coating of this Example, in contrast, the transmission of a CO_2 laser beam was maintained at the initial value of 99 % or more for one month or longer under the same standing conditions.

Example 2

As shown in Fig. 1, the input and output end of a silver bromide crystal fiber 1 is provided with an anti-reflection coating consisting of an inner layer 2 of potassium chloride and a outer layer 3 of cadmium telluride by vacuum vapor deposition. It is apparent from Fig. 2 that the combination of potassium chloride with cadmium telluride having a refractive index of 2.67 at a wavelength of 10.6 μm, as the outer layer, results in a reflectivity of zero.

In this Example, the inner layer was provided at a thickness of 1.82 μm and the outer layer was provided at a thickness of 2.10 μm.

In this Example, not only was the potassium chloride of inner layer 2 protected from decomposition due to water by the cadmium telluride of outer layer 3 in a similar manner to Example 1, but also the silver bromide crystal of substrate fiber 1 was protected from decomposition due to visible rays and ultraviolet rays. That is, cadmium telluride of outer layer 3 has a transmitting wavelength region of 0.9 to 15 μm and is opaque to visible rays and ultraviolet rays, and so incident visible rays or ultraviolet rays are intercepted by outer layer 3 and no decomposition of the silver bromide crystal of substrate fiber 1 occurs attributable to visible rays or ultraviolet rays. Thus, this anti-reflection coating can not only maintain the initial performance against moisture for a long period of time, but also serves as a filter cutting out visible rays and ultraviolet rays from the substrate material.

Comparative data for this Example compared with a monolayer coating of potassium chloride are as follows:

When allowed to stand in a humidity of 60 % at room temperature for a long time in an analogous manner to Example 1, the double layer coating of this Example maintained the transmission of a CO_2 laser beam at the initial value of 99 % or more for one month or longer.

When the input and output end of a silver bromide crystal fiber 1 coated with potassium chloride/cadmium telluride films according to the present invention was allowed to stand in the open air with fine weather for one day, there was no change in the transmission of a CO_2 laser beam while in the case of another silver bromide crystal fiber coated with a monolayer coating of potassium chloride for comparison purposes, the silver bromide crystal was sensitized by the visible rays and ultraviolet rays of the sunlight and turned black thus lowering the transmission of a CO_2 laser beam to 20% after being allowed to stand for two hours under similar conditions.

Example 3

The stability of anti-reflection coatings for infrared transmitting materials, obtained in an analogous manner to Example 1 except for changing the materials of the substrate, inner layer and outer layer as shown in Table 4, was examined, thus obtaining the results shown in Table 4:

Table 4

Substrate	Inner Layer (Film Thickness)	Outer Layer (Film Thickness)	Stability* to Water	Stability** Visible Rays & Ultraviolet Rays
KRS-5	NaCl (1.78 μm)	AgCl (2.68 μm)	O	
		KRS-5 (2.23 μm)	O	
		PbF_2 (2.57 μm)	△	
		Ge (1.3 μm)	O	O
	KBr (1.73 μm)	GaAs (1.7 μm)	O	O
	KCl (1.83 μm)	AgBr (2.41 μm)	O	
		ZnS (2.41 μm)	△	
		Si (1.63 μm)	O	O
		KRS-6 (2.44 μm)	O	
		AgCl (2.68 μm)	O	
		KRS-5 (2.23 μm)	O	
AgBr	KCl (1.83 μm)	Ge (1.3 μm)	O	O
KRS-6		GaAs (1.7 μm)	O	O
		AgBr (2.41 μm)	O	
		ZnS (2.41 μm)	△	
		Si (1.63 μm)	O	O
		KRS-6 (2.44 μm)	O	
CsI	NaF (2.2 μm)	Ge (1.3 μm)	O	O
		GaAs (1.7 μm)	O	O
		AgCl (2.68 μm)	O	
		AgBr (2.41 μm)	O	
		ZnS (2.41 μm)	△	
		Si (1.63 μm)	O	O
		ZnSe (2.19 μm)	O	

Note: *) Mark ○ means no change in transmission of CO_2 laser beam after standing in humidity of 60 % at room temperature for 1 month or longer. (initial transmission: 99 % or more)

Mark △ means no change in transmission of CO_2 laser beam after standing under same conditions for 1 week or longer. (initial transmission: 99 % or more)

**) Mark ○ means no change in transmission of CO_2 laser beam after standing in open air with fine weather for 2 hours. (initial transmission: 99 % or more)

As illustrated above in detail, an anti-reflection coating for an infrared transmitting material, which is stable to water or moisture and free from deterioration in performance for a long period of time, can be formed according to the present invention and, moreover, an anti-reflection coating for an infrared transmitting material can be provided which is capable of intercepting visible rays and ultraviolet rays as a filter thus preventing decomposition of a substrate material.

CLAIMS:

1. An anti-reflection coating for an infrared transmitting material, comprising an inner layer of an alkali metal halide and, provided on the inner layer, an outer layer of an infrared transmitting material, the inner layer and outer layer being provided on a substrate of the infrared transmitting material and having refractive indexes within the valves of the shaded portion of the accompanying Figure 2, n being the refractive index of the substrate.

2. A coating as claimed in claim 1, wherein the substrate is a crystalline plate or fiber.

3. A coating as claimed in claim 1 or claim 2,wherein the infrared transmitting material of the substrate is a silver halide, a thallium halide, or an alkali metal halide.

4. A coating as claimed in claim 3, wherein the substrate material is selected from silver bromide, silver chloride and mixed crystals thereof, thallium chloride, thallium bromide, thallium iodide and mixed crystals thereof, cesium iodide or cesium bromide.

5. A coating as claimed in any one of claims 1 to 4, wherein the alkali metal halide of the inner layer is potassium bromide, potassium chloride, sodium chloride, sodium fluoride, or mixed crystals thereof.

6. A coating as claimed in any one of claims 1 to

5, wherein the infrared transmitting material of the outer layer is silver bromide, silver chloride or mixed crystals thereof, thallium chloride, thallium bromide, thallium iodide or mixed crystals thereof, lead fluoride, zinc sulfide or zinc selenide.

7. A coating as claimed in any one of claims 1 to 5, wherein the infrared transmitting material of the outer layer is germanium, silicon, cadmium telluride or gallium arsenide.

8. A coating as claimed in any one of claims 1 to 7, wherein the inner layer and the outer layer have been coated onto the substrate by vapor deposition.

9. A laser beam transmitting window or fiber incorporating a coating as claimed in any one of claims 1 to 8.

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FIG. 1

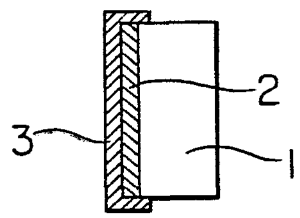
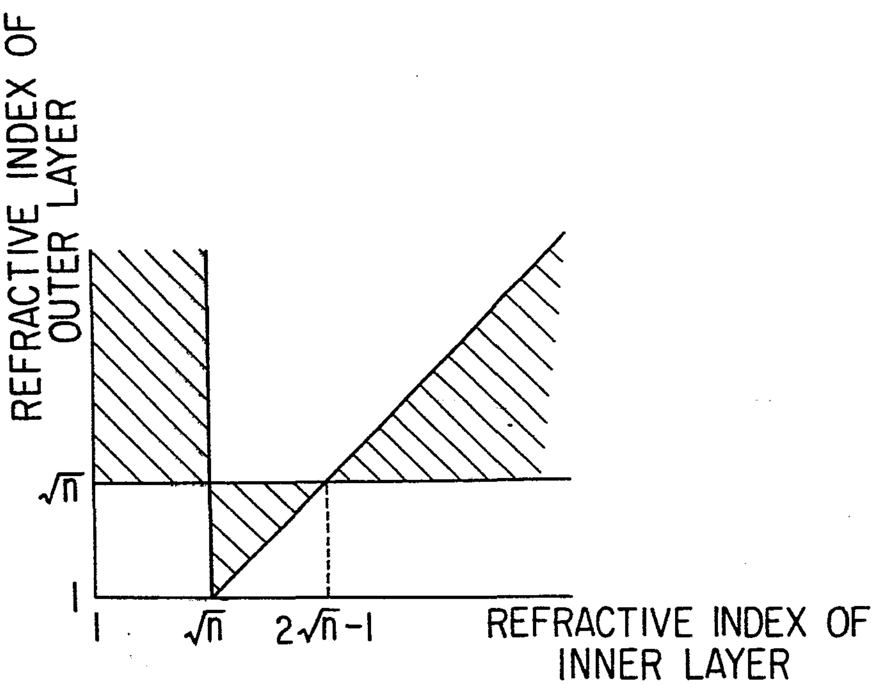

2
3
1

FIG. 2


REFRACTIVE INDEX OF OUTER LAYER
√n
1
1
√n
2√n-1
REFRACTIVE INDEX OF INNER LAYER